AD A107049

Special Report 81-15

July 1981

LEVEL II

12

LIMNOLOGICAL INVESTIGATIONS: LAKE KOOCANUSA, MONTANA

PART 5: PHOSPHORUS CHEMISTRY OF SEDIMENTS

I.K. Iskandar and S.S. Shukla

DTIC FILE COPY

DTIC
ELECTE
NOV 10 1981
S D
D

Prepared in cooperation with
U.S. ARMY ENGINEER DISTRICT, SEATTLE
By

UNITED STATES ARMY CORPS OF ENGINEERS
COLD REGIONS RESEARCH AND ENGINEERING LABORATORY
HANOVER, NEW HAMPSHIRE, U.S.A.

CRREL

Approved for public release; distribution unlimited.

81 11 09 174

FOREWORD

The Kootenai River basin, Libby Dam and the resulting Lake Koocanusa have been of interest to CRREL investigators since the mid-1970's. We have focused on a number of cold regions remote sensing, water quality, and limnological problems. Of particular interest are those associated with winter ice cover, spring snowmelt runoff, and low temperature chemical reactions in sediments and in the water column. Since CRREL and the Seattle District have conducted a number of short and long term studies on the Kootenai River and Lake Koocanusa, we considered it appropriate to make the results of those investigations readily available in a series of reports. Therefore, we are issuing these results in the CRREL Special Report series under the overall title *Limnological investigations: Lake Koocanusa, Montana.*

Part 1: Pre-impoundment study: 1967–1972, with appendix, *Basic data*

Part 2: Environmental analyses in the Kootenai River region, Montana (Reprint of CRREL Special Report 76-13)

Part 3: Basic data, post-impoundment: 1972–1978

Part 4: Factors controlling primary productivity

Part 5: Phosphorus chemistry of sediments

Cover: Libby Dam and Lake Koocanusa, Montana, 1975. (Photograph by U.S. Army Engineer District, Seattle.)

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

(9) 1. REPORT NUMBER: Special Report 81-15

2. GOVT ACCESSION NO.: AD-A107049

3. RECIPIENT'S CATALOG NUMBER:

(6) 4. TITLE (and Subtitle): LIMNOLOGICAL INVESTIGATIONS: LAKE KOOCANUSA, MONTANA. PART 5. PHOSPHORUS CHEMISTRY OF SEDIMENTS

5. TYPE OF REPORT & PERIOD COVERED: (14) CRREL-SR-81-15

6. PERFORMING ORG. REPORT NUMBER:

(10) 7. AUTHOR(s): I.K. Iskandar [redacted] S.S. Shukla

8. CONTRACT OR GRANT NUMBER(s): (16)

9. PERFORMING ORGANIZATION NAME AND ADDRESS: U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire 03755

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: CWIS 31111 and DA Project 4A161101A91D, ILIR Work Unit FY79(298)/FY80(308)

11. CONTROLLING OFFICE NAME AND ADDRESS: Office of the Chief of Engineers, Washington, D.C. 20314

12. REPORT DATE: (11) Jul[redacted]81

13. NUMBER OF PAGES: 14 (12) 14

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office):

15. SECURITY CLASS. (of this report): Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Lakes
Lake eutrophication
Phosphorus
Phosphorus sink
Sediments

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This study characterizes the sediments from Lake Koocanusa (Libby Dam reservoir), Montana, in terms of their ability to sorb and release P. Sediment samples were collected at 12 stations located between the U.S.–Canadian border and Libby Dam (42 miles downstream of the border) during July 1977. The sediments from Lake Koocanusa are calcareous, low in organic matter (< 2.3%), and have a silty loam or loam texture. Most of the P associated with these sediments was in the inorganic form (> 85%), which was highly correlated (r = 0.89) with oxalate extractable Fe in the sediment. Sorption tests, with concentrations of either 1000 or 10,000 µg P/g sediments, showed that these sediments have limited ability to sorb additional P from concentrated solutions. The maximum amount sorbed at the lower P → next page

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

micrograms

Unclassified 037100

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. Abstract (cont'd)

concentrations was 67% of the added P and was highly correlated with oxalate extractable Fe in the sediments. Desorption studies showed that very small amounts of both the originally bound P (1 to 2%) and the added P (< 6.3%) were released. Conclusion: the sediments in Lake Koocanusa act as a P sink.

PREFACE

This report was prepared by Dr. I.K. Iskandar, Research Chemist, Earth Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory and Dr. S.S. Shukla, formerly of the Department of Soil Science, University of Wisconsin, Madison. The study was supported by the Corps of Engineers Civil Works Program, *Environmental Quality/Environmental Impact;* Subprogram, *Cold Regions Environmental Impact;* Work Unit CWIS 31111, *Environmental Criteria for Resource Management in Cold Regions* and by DA Project 4A161101A91D, *In-House Laboratory Independent Research;* Work Unit FY79 (298)/FY80 (308), *Sediments as Buffers and Sinks of Nutrients in Cold Regions Water Bodies.*

The authors express their appreciation to Dr. J. Brown, Chief, Earth Sciences Branch, CRREL, for arranging financial support for the initial stages of the project; R. Bush, U.S. Army Engineer District, Seattle, who arranged the field trip for sampling; and M. Briggs, Libby Dam, who provided assistance with sampling locations and background information on the terrain before and after construction. S.G. Halaka of the University of Wisconsin, Madison, is also gratefully acknowledged for analyzing some of the samples. This report was technically reviewed by J. Helms, Hydrology and Hydraulics Branch; P. Storm and R. Bush, Environmental Resources Section, U.S. Army Engineer District, Seattle; and Dr. J.E. Hobbie, CRREL Consultant, Marine Biological Laboratory, Woods Hole, Massachusetts.

The contents of this report are not to be used for advertising or promotional purposes. Citation of brand names does not constitute an official endorsement or approval of the use of such commercial products.

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	

DTIC ELECTE NOV 10 1981 S D

LIMNOLOGICAL INVESTIGATIONS: LAKE KOOCANUSA, MONTANA

PART 5: PHOSPHORUS CHEMISTRY OF SEDIMENTS

I.K. Iskandar and S.S. Shukla

INTRODUCTION

Libby Dam is situated in the northwestern part of Montana, and it forms a reservoir with a gross water storage capacity of 5,809,000 acre-ft at a normal full-reservoir elevation of 2459 ft above mean sea level. The Corps of Engineers began construction of Libby Dam in the spring of 1966 and completed the impoundment of the Kootenai River in March 1972. The resulting reservoir (named Lake Koocanusa) occupies a long, narrow valley between steeply sloping mountains. These surrounding mountains are rocky, with a scant soil cover, but have a fairly thick vegetative cover, primarily composed of pine trees. The rocks are metamorphic, with siltstone the most extensive. Sonar fathometer runs show the steep slopes of the old mountains on the bottom of both sides of the reservoir, with occasional sites having flat benches.

A preimpoundment study of the river (Bonde and Bush 1975) found nutrient concentrations and loadings to be sufficiently high to predict the development of a eutrophic lake after impoundment. The prediction seems to be accurate because during the fall of 1974 and late summer and fall of 1975 extensive blue-green algal blooms were observed in the lake (Hobbie 1976, Bush and Bonde 1977).

The reservoir is a recent man-made lake in an area which has a low in situ native soil cover. It has a very low sedimentation rate, primarily because of a very low sediment load that is believed to be about 1,000 acre-ft/year.

Since 1972, the Seattle District of the Corps of Engineers, through contracts with the U.S. Geological Survey, the University of Montana and the University of Idaho, has been collecting water quality and limnological data from several locations in the lake.

During the period 15-17 August 1977 a multidisciplinary team from CRREL, the Seattle District, the U.S.G.S., the Montana Department of Fish and Game, the University of Idaho, the Marine Biological Laboratory (Woods Hole, Massachusetts), and the University of Wisconsin (Madison) conducted an intensive in-lake study. The objective was to gain information on lake processes that would help in interpreting the data obtained from routine analyses over the past years. Previous monitoring efforts centered mainly on the water column, with very limited data gathered on sediment composition or the chemistry of the sediment/water interface. Phosphorus (P) is usually considered the limiting factor in open water eutrophication (Lee et al. 1978) and sediments generally control (as a buffer or sink) P levels in the overlying water. Previous analyses of Lake Koocanusa sediments included only total P, which does not reflect the nature of its binding and availability for aquatic plants. Variation over time of total P in sediments from the same location was reported to be extremely large (data from October 1972 and June 1973 at the border station were reported to be 720 and 13 μg P/g sediment respectively).

The objectives of this report are to discuss the nature of P in sediments from selected locations

in Lake Koocanusa, to correlate the amounts and forms of P found to other sediment characteristics, and to assess the potential eutrophic status of the lake if P is the limiting factor.

MATERIALS AND METHODS

Sediment collection

Initially, sediment samples were collected along length and width cross sections of the lake at the established water quality stations. However, sediment sampling along the width cross sections did not yield sufficient material because of a lack of soft bottom sediments, even on some of the flat benches. As a consequence, samples were collected along longitudinal traverses of the old Kootenai River channel at more places than the established water quality stations.

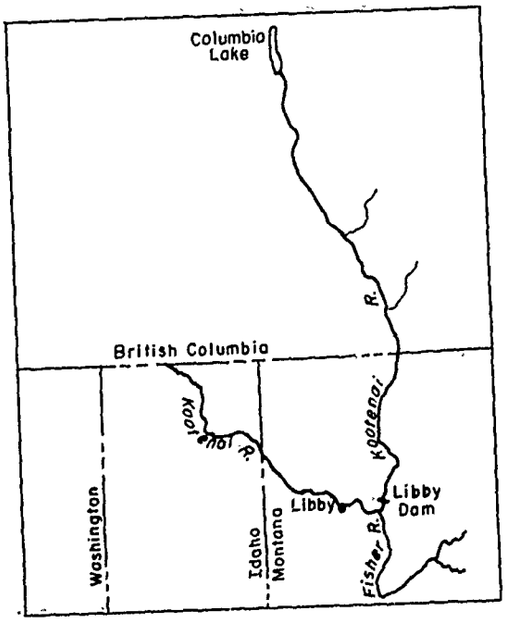
A total of 12 longitudinal stations were selected between the dam site (Forebay area) and the U.S.-Canadian border, a distance of approximately 42 miles (Fig. 1 and Table 1). Sonar was extremely helpful in locating the old river channel, which was the only assured place for collecting sediments from this relatively deep reservoir. Most of the lake bottom is too steep for sediment deposition. General procedure was to first sample the shallower flat benches (located by sonar), and if unsuccessful, this was followed by sampling the old river channel.

Twenty sediment samples were collected on 16 and 17 August 1977 using a Ponar dredge. Table 1 lists the sampling location, depth, and approximate distance from reservoir banks. After collection, the samples were sealed in glass containers and stored at 4°C.

Sample preparation and analysis

The sediments were well mixed with a plunger before subsamples from the glass containers were analyzed. The weight of solids in the bulk samples was determined by drying at 110°C overnight.

Short-range order (amorphous) hydrous Fe and Al oxides were extracted by acid ammonium oxalate (Saunders 1965), and are hereafter referred



a. General location of lake.

b. Area immediately around lake.

Figure 1. Location of Lake Koocanusa.

Table 1. Location of sediment samples.

Sample number	Location	Depth (ft)	Approximate distances: Overall width (ft)	Approximate distances: Distance from shore* (ft)
1	Upstream of Tobacco River (Canadian border)	114	6000	1000 E
2	Upstream of Tobacco River	132	6000	M
3	Tobacco River (mouth)	120	6000	600 W
4	¼ mile south of Rexford bench	129	6500	M
5	¼ mile south of Rexford bench	132	6500	150 E
6	¼ mile south of reservoir bridge	184	4500	350 W
7	½ mile north of Sutton Creek	156	4000	275 E
8	½ mile north of Sutton Creek	186	4000	M
9	1000 ft north of Big Creek	168	4000	300 W
10	1000 ft north of Big Creek	192	4000	M
11	½ mile south of Parsnip Creek	216	3500	900 W
12	½ mile south of Parsnip Creek	198	3500	M
13	Ten Mile Creek	160	6500	M
14	Ten Mile Creek	235	6500	M
15	Five Mile Creek	165	6000	2000 E
16	Barron Creek	170	5200	1000 E
17	Barron Creek	270	5200	350 W
18	Yarnell Island	282	4400	300 E (off island)
19	Forebay	256	3200	M
20	Forebay (straight from moorage)	304	3200	2400 W

*E — Approximate distance from the East bank.
W — Approximate distance from the West bank.
M — Middle

to as Ox-Fe, Ox-Al and Ox-P. The Fe, Al and P were determined in oxalate extracts after destroying the oxalate by oxidation with HNO_3-HCl on a sand bath followed by ignition at 450°C. The Ox-Fe and Ox-Al were determined by the Ferron method (Rainwater and Thatcher 1960), and Ox-P by the phosphomolybdate method (Murphy and Riley 1962).

The total and inorganic P in the sediments were extracted by the method of Mehta et al. (1954), converted to ortho-P and determined by the phosphomolybdate method (Murphy and Riley 1962). Organic P was calculated by subtracting inorganic P from total P.

The pH of the sediments was measured by pH electrode, and the $CaCO_3$ concentration determined by a manometric procedure (Leo 1963). Organic C was determined by oxidation with H_2SO_4-$K_2Cr_2O_7$ (Walkley and Black 1934), and a factor of 1.72 was used to convert organic C to organic matter (this factor is customarily used by soil scientists).

Samples were pretreated for textural analysis by oxidizing organic matter with H_2O_2, followed by dispersion of mineral matter with Calgon (sodium hexametaphosphate). The texture of the resultant sediment mineral dispersion was determined by use of a calibrated hydrometer (Bouyoucos 1927).

To assess the ability of the sediment to sorb or release added inorganic P, a series of experiments were conducted in the laboratory. For the sorption study, an equivalent volume of wet sediment containing 1 g of dry-weight sediment was placed in a centrifuge tube and diluted to bring the weight of the liquid phase to 25 g. Then 25 ml of 0.2 M NaCl, containing the desired amounts of inorganic P as KH_2PO_4, was added. The samples were shaken on an end-over-end shaker for 24 hr at 25°C, centrifuged, and then an aliquot of the supernatant was taken for the determination of the equilibrium P concentration using the phosphomolybdate method of Murphy and Riley (1962). The quantity of P sorbed was then calculated from the difference between P added and P remaining in solution. Two levels of added P were used: 1000 µg P/g and 10,000 µg P/g of dry sediments. Desorption studies were conducted to evaluate the potential release of original and added inorganic P. Desorption of original P was

determined by equilibrating for 24 hr a wet sediment sample containing 1 g of dry weight sediment in a total of 50 ml of a 0.1 M NaCl solution. Desorption studies of added P were conducted by centrifuging the samples used for the sorption studies, decanting the supernatant, and weighing the samples for the determination of the water trapped in the sediments. Desorption studies of added P were similar to those for the originally bound P; however, the total amount of P desorbed was obtained by subtracting the amount of P in the trapped water from the amount of P in the supernatant after the desorption.

Results in this report are expressed on a dry-weight basis of the sediment, either as μg/g sediment or as percentages.

RESULTS AND DISCUSSION

At the time of sampling, Lake Koocanusa appeared to be a clear, deep-water, oligotrophic reservoir.

The sediments from the lake are calcareous, with a $CaCO_3$ concentration ranging from 6.3 to 27.4%, and a mean of 17.8 ± 5.1% (Table 2). There was no distinct correlation between percent $CaCO_3$ and depth of sediment deposition. The physicochemical properties of the Lake Koocanusa sediments (pH, percent $CaCO_3$, organic matter and textural types) are given in Table 2. Buffering by $CaCO_3$ is evidenced by the uniform and neutral pH of all the sediments (Table 2).

The organic matter content of the sediments is generally quite low, ranging from 0.47 to 2.3% with a mean of 1.08 ± 0.41%. The low organic content of these sediments is suggestive of a low lake productivity but may also be the result of small organic loads entering the lake. The higher levels of organic content were found in samples taken from the middle of the reservoir at the deeper locations.

Texturally, silt is the largest mineral fraction in most of the sediments which were silty clay. Sediments collected from middle stretches of the lake (the old river channel) are silty clay, as would be expected due to natural grading and settling. It is important to note that the parent material for these sediments is siltstone, and this probably influences the texture of the bottom sediments more than the low sediment load brought into the lake.

From a material balance standpoint, it appears that the organic and mineral matter in these sediments reflect the composition of the native material in the original bed and surrounding watershed areas, with limited addition from lacustrine sources, i.e. additional mineral

Table 2. Physicochemical properties of sediments.

Sample number	pH	$CaCO_3$ (%)	Org. matter (%)	Sand (%)	Silt (%)	Clay (%)	Texture
1	6.9	20.0	0.47	48	36	16	Loam
2	6.7	18.6	1.17	14	66	20	Silt loam
3	6.8	21.5	0.80	20	62	18	Silt loam
4	6.9	26.9	1.20	10	61	29	Silty clay loam
5	7.0	27.4	0.50	38	47	15	Loam
6	6.9	23.5	1.06	8	48	44	Silty loam
7	6.9	17.1	0.90	34	38	28	Clay loam
8	7.1	20.0	1.05	26	38	36	Clay loam
9	6.95	14.2	1.27	18	48	34	Silty clay loam
10	6.9	23.0	1.09	8	52	40	Silty clay
11	6.95	18.6	1.48	12	50	42	Silty clay
12	6.75	17.1	2.30	16	44	40	Silty clay
13	7.20	12.7	1.15	6	52	42	Silty clay
14	7.15	16.1	1.39	4	52	44	Silty clay
15	6.9	14.7	1.48	10	44	46	Silty clay
16	7.15	18.1	0.82	18	58	24	Silty loam
17	7.20	11.7	1.09	34	32	34	Loam
18	7.0	16.6	0.74	20	50	30	Silty clay loam
19	7.2	11.2	1.07	—	—	—	—
20	7.0	6.3	0.50	16	59	25	Silt loam

matter from sediment deposition and additional organic matter from the growth, decay and deposition of benthic or floating flora and fauna.

Inorganic P constitutes most of the P present in these sediments, ranging from 87 to 98% of the total P present, the remaining portion being organic P (Table 3). Lower levels of organic P could partly be explained by the low organic matter content of these sediments. Since the lake is in an isolated area, the source of high levels of inorganic P in these sediments could be the decomposition of native rocks or enrichment from the discharge of P-containing wastes from the fertilizer plant in Canada. Results of the study of the overlying water column suggest the latter reason; however, this is not confirmed by the difference in the longitudinal distribution of P from the U.S.-Canadian border to Libby Dam. The concentration of P would be expected to be higher in the sediments from near the U.S.-Canadian border (sample number 1) and then decrease with distance towards the Forebay area of Libby Dam (sample number 20). Analysis of the sediments collected shows no such trend. Since only the U.S. portion of the lake was sampled and the lake extends approximately 46 miles into Canada at full pool, the P from the fertilizer plant may have been deposited within the Canadian portion of the lake. Additional work needs to be done to establish the background of P in the surrounding watershed and P in the sediments in Canada for a better understanding of P dynamics.

Samples taken from a cross section across the width of the lake showed both the inorganic and total P concentrations to be higher in sediments from deeper sites (old Kootenai River channel) than in sediments from shallow benches. This may be due to higher P loading in the old river channel, or to the deposition of sediment by natural grading, where P could have originated from the fertilizer manufacturing waste or runoff from the watershed. Since most ortho-P is a highly reactive compound, it is quite likely that most of the P waste has been sorbed by the sediment within short distances from the fertilizer waste source in Canada.

There is more Ox-Fe than Ox-Al in all the samples extracted with acid ammonium oxalate (Table 3). This reagent also extracted 61 to 97% of the total inorganic P, except in samples 1 and 5, which are coarse sediments from shallow areas that also contained the lowest amounts of Ox-Fe. High removal of inorganic P by oxalate agrees with other studies of lake sediments (Williams et al. 1971) and is substantiated by a good correlation ($r = 0.89$) between Ox-P and total inorganic P (Table 4).

The ability of acid ammonium oxalate to remove short-range-order Fe and Al from lake sedi-

Table 3. Phosphorus and oxalate extractable Fe, Al, and P (μg/g).

Sample number	Phosphorus			% inorg. P of total	Oxalate extractable				% Ox-P of total inorg. P
	Total inorg.	Total org.	Total		Inorg P	Fe	Al	Fe + Al	
1	750	50	800	94	200	1310	100	1410	27
2	950	50	1000	95	700	5800	1090	6890	74
3	750	50	800	94	400	3200	620	3820	53
4	950	50	1000	95	700	4700	1050	5750	74
5	700	50	750	93	220	1700	580	2280	31
6	1000	125	1125	89	780	5300	800	6100	78
7	850	25	875	97	520	4500	330	4830	61
8	850	25	875	97	660	4300	360	4660	78
9	950	50	1000	95	700	7500	440	7940	74
10	1100	25	1125	98	760	7900	360	8260	69
11	1200	50	1250	96	1060	10,900	1380	12,280	88
12	1300	75	1375	94	900	10,000	1640	11,640	69
13	1050	125	1175	89	920	7600	1130	8730	88
14	1350	150	1500	90	1080	10,000	1450	11,450	80
15	1300	150	1450	90	1060	13,200	440	13,640	82
16	850	125	975	87	520	5300	980	6280	61
17	1210	165	1375	88	848	7200	980	8180	70
18	1000	125	1125	89	800	9700	1300	11,000	80
19	950	50	1100	95	920	7900	1670	9570	97
20	850	25	875	97	648	3700	950	4650	76

Table 4. Simple linear regression and correlation coefficients indicating degree of relationship between P and other sediment parameters.

	Parameters tested	*Regression equation*	*Correlation coefficient*
1	Ox-P with Ox-Fe	Ox-P = 0.072 Ox-Fe + 245.65	0.90
2	Ox-P with Ox-Al	Ox-P = 0.327 Ox-Al + 430.93	0.60
3	Ox-P with Ox-(Fe+Al)	Ox-P = 0.068 Ox-(Fe+Al) + 212.08	0.92
4	Ox-P with total inorganic P	Ox-P = 1.154 total P_i* - 429.09	0.89
5	Total inorganic P with Ox-Fe	Total P_i = 0.54 Ox-Fe + 637.36	0.89
6	Total inorganic P with Ox-(Fe+Al)	Total P_i = 0.051 Ox-(Fe+Al) + 618.50	0.89
7	Total inorganic P with %$CaCO_3$	Total P_i = -10.414 (%$CaCO_3$) + 1180.51	-0.28
8	Ox-P with %$CaCO_3$	Ox-P = -20.27 (%$CaCO_3$) + 1079.91	-0.42

*P_i = total inorganic P

ments and the importance of these compounds in forming the P-sorbing complex has been reported by Shukla et al. (1971). As indicated by correlation coefficients (Table 4) for different sediment parameters, the sediment of Lake Koocanusa also emphasizes the importance of Ox-Fe and Ox-(Fe+Al) in sorbing P in lake sediments.

Although the amount of $CaCO_3$, which has the ability to sorb added P, far exceeds the amount of Ox-Fe and Ox-(Fe+Al), correlation analysis does not show $CaCO_3$ to be responsible for the sorption of P in these lake sediments; i.e., the variability in $CaCO_3$ does not account for any variation in inorganic P. In fact percent $CaCO_3$ has a negative low correlation (Table 4) with both total inorganic P (r = -0.28) and Ox-P (r = -0.42). Similar results were noted by Williams et al. (1971).

On a single component basis, Ox-Fe is well correlated to both total P (r = 0.89) and Ox-P (r = 0.92). Table 4 summarizes the relationships among various sediment parameters studied in this report.

Inorganic P in lake sediments can exist as "occluded" and "nonoccluded" forms, describing whether the P is contained in a mineral matrix or is associated with amorphous or metastable complexes present in the sediment respectively. Unless P is removed by precipitation as a function of the solubility product of different ions present in any given lake system (e.g., Ca, Fe and Al in general), the removal mechanism can be envisioned as surface sorption on different sediment components constituting the nonoccluded form. From the nonoccluded form, the occluded form can develop over a period of time by either the slow processes of diffusion or by having a fresh coating over the surfaces which sorbed P.

Calcareous sediments in Wisconsin have been reported to show limited ability to remove P by $CaCO_3$ (Shukla et al. 1971, Williams et al. 1971) where Ox-Fe appeared to be better correlated with native P as well as the determining factor in the removal of added ortho-P from the aqueous phase. As already mentioned and shown in Table 4, this also seems to be the case for the calcareous sediments of Lake Koocanusa, where Ox-Fe appears to be the dominating parameter as far as its relationship with native P is concerned. Further studies with and without Ox-Fe in these sediments would reveal the ability of these sediments to remove added ortho-P, as well as the relationship between Ox-Fe and Ox-(Fe+Al). By analogy to calcareous Wisconsin sediments, it does, however, appear that Ox-Fe would probably emerge as the single most important parameter governing the chemistry of inorganic P in Lake Koocanusa sediments.

Sorption studies

Table 5 summarizes the sorption data obtained from equilibrating sediment samples from Lake Koocanusa with 1000-µg P/g sediments and 10,000-µg P/g sediments. The data indicate that these sediments have a limited ability to sorb added inorganic P. When 1000 µg of P was added per g of sediment, the maximum P sorbed was 68.9% and the minimum was 22.6%. At the higher level of P addition, those values were 18 and 3.6% respectively.

Table 5. Sorption of inorganic P by sediments from Lake Koocanusa at two levels of added P.

Sample number	1,000 µg P/g sediments		10,000 µg P/g sediments		Native inorganic P (µg/g)
	µg P sorbed/ g sediment	% of added P sorbed	µg P sorbed/ g sediment	% of added P sorbed	
1	254	25.4	500	5.0	750
2	471	47.1	400	4.0	950
3	—	—	—	—	—
4	358	35.8	750	7.5	950
5	226	22.6	361	3.6	700
6	396	39.6	600	6.0	1000
7	415	41.5	650	6.5	850
8	321	32.1	600	6.0	850
9	449	44.9	1150	11.5	950
10	490	49.0	1300	13.0	1100
11	622	62.2	1100	11.0	1200
12	689	58.9	1400	14.0	1300
13	—	—	—	—	—
14	585	58.5	1750	17.5	1350
15	—	—	—	—	—
16	377	37.7	1050	10.5	850
17	481	48.1	1300	13.0	1210
18	556	55.6	1800	18.0	1000
19	—	—	—	—	—
20	283	28.3	1200	12.0	850

As discussed earlier, Ox-Fe appears to be the dominating component determining the ability of sediments to sorb added inorganic P. At both levels of P additions, a higher proportion of added P was sorbed by sediment samples 11, 12, 14 and 18, which also had higher amounts of Ox-Fe (Table 3). Lower amounts of Ox-Fe in sediment samples 1 and 5 correspond to a lower content of sorbed P in those sediments. At the 1000-µg P addition, good correlation ($r = 0.96$) between added P sorbed and sediment Ox-Fe was found. For the 16 sediment samples studied, this relationship may be described by

$$\% \text{ P added sorbed} = 0.0044\ (\mu g \text{ Ox-Fe/g sediment}) + 16.46.$$

In contrast there was a negative relationship between P sorbed and $CaCO_3$ content of the sediment ($r = -0.21$). In this context $CaCO_3$ acts as a diluting factor for the sediment's ability to sorb P.

The ability of the sediments from Lake Koocanusa to sorb added inorganic P did not change significantly with increasing concentrations of added P. The maximum increase in P sorption, when the amounts of P added increased 10-fold, was noticed with sample 18. In this case a three-fold increase was observed that probably was due to a lower initial inorganic P content.

Desorption studies

Table 6 shows the amounts of P desorbed (released) from Lake Koocanusa's sediments under different initial conditions. Very small amounts of initial P were desorbed from these sediments (1 to 2%). Although some sediments sorbed considerably higher amounts of inorganic P than they originally contained, there was only a slight increase in the amount of P desorbed (Table 6). Furthermore, the amount of P desorbed was similar after both levels of P sorption, despite the fact that generally higher amounts of P were sorbed at 10,000 µg P/g than at 1000 µg P/g (Table 5). This indicates that the sediments acted as a P sink.

Table 6. Inorganic P desorption characteristics of sediments from Lake Koocanusa.

Sample number	Native P		Equilibrium with 1000 µg P/g sediment		Equilibrium with 10,000 µg P/g sediment	
	Desorbed P µg/g sed.	Percent desorption	Desorbed P µg/g sed.	Percent desorption	Desorbed P µg/g sed.	Percent desorption
1	7	0.9	48	4.8	20	0.6
2	12	1.3	58	4.1	34	2.5
3	—	—	—	—	—	—
4	12	1.3	69	5.2	69	3.5
5	6	0.9	55	5.5	67	6.3
6	14	1.4	78	5.6	36	2.2
7	8	0.9	59	4.7	82	5.5
8	18	2.1	95	7.3	82	5.7
9	12	1.1	66	4.9	75	3.6
10	8	0.7	58	4.1	63	2.6
11	16	1.5	67	3.4	77	3.4
12	6	0.5	69	3.6	95	3.5
13	—	—	—	—	—	—
14	16	1.2	67	3.5	41	1.3
15	—	—	—	—	—	—
16	10	1.2	69	5.2	64	3.4
17	18	1.5	70	5.1	74	3.0
18	12	1.2	59	4.8	7	0.4
19	—	—	—	—	—	—
20	14	1.7	61	5.4	45	2.2

CONCLUSIONS

1. In Lake Koocanusa sediment deposition appears to be limited, with accumulation occurring only on certain flat bottoms, particularly the old Kootenai River channel.

2. The sediments are fine textured with high concentrations of silt and $CaCO_3$.

3. The sediments have a low organic matter content and have neutral pH.

4. The sediments of Lake Koocanusa are characteristic of those of oligotrophic lakes.

5. The distribution of P in the sediments along the longitudinal section of the lake does not clearly reflect the effects of P inflow from Canada.

6. Despite relatively high amounts of $CaCO_3$ in the sediments, no relationship between $CaCO_3$ and the inorganic P in the sediments can be shown.

7. It appears that most of the inorganic P is associated with the Ox-Fe and Ox-Al fractions of the sediments, generally believed to be highly reactive short-range-order complexes.

8. The sediments from Lake Koocanusa have limited ability to sorb added inorganic P. Sorption of added P increased slightly with increasing concentrations but was not significant in most cases.

9. The sediments from Lake Koocanusa showed very little ability to release (desorb) inorganic P and may be considered a sink.

REFERENCES

Bonde, T.J. and R.M. Bush (1975) Kootenai River water quality investigations—Libby Dam preimpoundment study (1967–1972) Department of the Army, Seattle District, Corps of Engineers.

Bush, R.M. and T.J. Bonde (1977) Relating water quality to the aquatic environment: Libby Dam-Lake Koocanusa Project case study. *Proceedings of a Seminar on Water Quality Data Collection and Management, 25–26 Jan 77, Denver, Colorado.* U.S. Army Corps of Engineers.

Bouyoucos, G.J. (1927) The hydrometer as a new method for the mechanical analysis of soils. *Soil Science*, vol. 25, p. 343–352.

Hobbie, J.E. (1976) Limnology of Lake Koocanusa, Montana In *Environmental analyses in the Kootenai River region, Montana.* U.S. Army Cold Regions Research and Engineering Laboratory, Special Report 76-13, ADA-033500.

Lee, G.F., W. Rast, and R.A. Jones (1978) Eutrophication of water bodies: Insights for an age-old problem. *Environmental Science and Technology*, vol. 12, p. 900–908.

Leo, M.W.M. (1963) Determination of soil carbonates by a rapid gasometric method. *Journal of Agriculture and Food Chemistry*, vol. 11, p. 452–455.

Mehta, N.C., J.C. Legg, C.A.J. Goring and C.A. Black (1954) Determination of organic phosphorus in soils. I. Extraction method. *Soil Science Society of America Proceedings*, vol. 18, p. 443–449.

Murphy, J. and J.P. Riley (1962) A modified single solution method of phosphate in natural water. *Analytica Chimica Acta*, vol. 27, p. 31–36.

Rainwater, F.H. and L.L. Thatcher (1960) Methods for the collection and analysis of water samples. U.S. Geological Survey, Water Supply Paper 1454, p. 97–100.

Saunders, W.M.H. (1965) Phosphate retention by New Zealand soils and its relationship to free sesquioxides, organic matter and other soil properties. *New Zealand Journal of Agricultural Research*, vol. 8, p. 30–57.

Shukla, S.S., J.K. Syers, J.D.H. Williams, D.E. Armstrong and R.F. Harris (1971) Sorption of inorganic phosphate by lake sediments. *Soil Science Society of America Proceedings*, vol. 35, p. 244–249.

Walkley, A. and I.A. Black (1934) An examination of the Degtarieff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Science*, vol. 37, p. 29–38.

Williams, J.D.H., J.K. Syers, S.S. Shukla, R.F. Harris and D.E. Armstrong (1971). Levels of inorganic and total phosphorus in lake sediments as related to other sediment parameters. *Environmental Science and Technology*, vol. 5, p. 1113–1120.

☆U.S. GOVERNMENT PRINTING OFFICE: 1981 — A-2076/155